Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of the European Ceramic Society 25 (2005) 829–836
www.elsevier.com/locate/jeurceramsoc

Paper derived biomorphic porous titanium carbide and titanium oxide ceramics produced by chemical vapor infiltration and reaction (CVI-R)

Nadja Popovska, Daniela Almeida Streitwieser*, Chen Xu, Helmut Gerhard

Department of Chemical Reaction Engineering, University of Erlangen-Nuremberg, Egerlandstrasse 3, Erlangen D-91058, Germany

Received 30 December 2003; received in revised form 25 March 2004; accepted 3 April 2004
Available online 20 June 2004

Abstract

Chemical vapor infiltration (CVI) is used for producing biomorphic porous TiC ceramics derived from paper. The paper samples are first carbonized in inert atmosphere to yield biocarbon template structures (C_b-template). Subsequently, three routes for converting the C_b-templates into TiC ceramics are studied. The first route includes CVI with $TiCl_4$-H_2. The effect of methane as additional carbon source is investigated on the second route ($TiCl_4$-H_2-CH_4). Finally, a two step CVI process (Route 3), first $TiCl_4$-H_2 and subsequent $TiCl_4$-H_2-CH_4, is performed in order to improve both the grade of conversion of the C_b-template into TiC and the mechanical properties of the resulting porous TiC ceramics. Furthermore, porous TiO_2 ceramics are produced by high temperature oxidation of the TiC ceramics in air flow.

Keywords: Porous ceramics; Biomorphic ceramics; TiC; Chemical vapor infiltration

1. Introduction

Biomorphic cellular ceramics are a new class of ceramic materials with natural designed porous structure having recently attained particular interest. They are obtained by carbonization and consecutive conversion of biological preforms into ceramics. During the conversion their microstructure is neither destroyed nor altered, only a homogeneous shrinkage in all directions takes place during carbonization.[1,2] Various biotemplate processing technologies are developed for manufacturing of biomorphic SiC-based ceramics. Among these methods the most investigated are the Si liquid infiltration,[3–5] the Si gas infiltration,[5–7] the SiO vapor infiltration,[6,8] the polymer infiltration[9] and, the method used in this paper, the CVI-R method.[10–13] Compared to the other infiltration methods the chemical vapor infiltration (CVI) has the advantage of using relatively low processing temperatures, retaining the initial structure of the biotemplate on a micrometer level. Biomorphic SiC porous ceramics could be applied as high temperature filters or catalytic support structures due to their high thermal conductivity, good oxidation and corrosion resistance as well as high strength at elevated temperatures.

The properties of porous TiC ceramics are inferior to those of SiC, however, their improved corrosion resistance in phosphoric acid, the high electrical conductivity as well as the very good wet ability by metal melts made these materials interesting candidates for specific applications such as ceramic–metal composites[14] or catalyst supports for chemical and biochemical reactions.[15,16] TiO_2 ceramics are used as catalysts in photochemical and in biochemical reactions, for example in the purification of water.[17,18]

There exist only few reports about production of porous TiC and TiO_2 ceramics. The infiltration of dried wood or charcoal with titanium tetra-isopropoxide, followed by high temperature treatment yields highly porous TiO_2 ceramics.[19,20] A porous TiC ceramic is prepared by liquid vacuum infiltration of wood derived carbon structures with tetrabutyl-titanat.[21] First, the tetrabutyl-titanat decomposes to TiO_2, and then reacts with the carbon biotemplate at temperatures of about 1400 °C forming TiC.[21] In[22] our first results about the processing of TiC porous ceramic from wood by chemical vapor infiltration are reported.

* Corresponding author. Tel.: +49 9131 852 7437; fax: +49 9131 852 7421.
E-mail address: daniela.almeida@rzmail.uni-erlangen.de (D.A. Streitwieser).

0955-2219/$ – see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2004.04.007

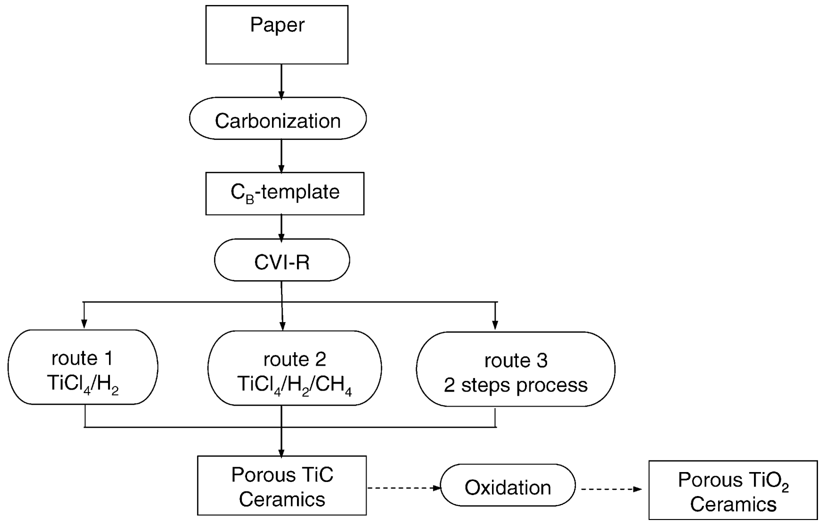

Fig. 1. Flow chart of the CVI-R ceramization process with three different routes.

In this study, chemical vapor infiltration-and reaction (CVI-R) process with $TiCl_4$-H_2 and $TiCl_4$-H_2-CH_4 systems is investigated to produce biomorphic cellular TiC ceramics by converting carbon fibers from paper biotemplates into TiC. The processing scheme is presented in Fig. 1. Three routes for converting the carbon biotemplates (C_b) into TiC ceramics are investigated. The first route includes chemical vapor infiltration with $TiCl_4$-H_2. The effect of methane as additional carbon source is investigated on Route 2. Finally, on the third route, two step CVI process is performed with $TiCl_4$-H_2 and subsequently with the $TiCl_4$-H_2-CH_4 system. The grade of conversion of the C_b-template into TiC as well as the mechanical properties of the resulting porous TiC ceramics should be improved with the two step process. Furthermore, first results on the processing of porous TiO_2 ceramics by oxidation of the TiC ceramics in air flow are presented.

2. Experimental procedure

The substrates used in this study are flat paper preforms of 0.80 mm thickness with a geometrical density of 0.22 g/cm^3. The initial porosity of the papers is 82% with a mean pore size of 25 μm. The papers are cut to 40 mm × 40 mm squares and carbonized at the conditions described below.

The carbonization of the paper performs and the chemical vapor infiltration of the resulting carbon biotemplates is performed in a horizontal hot-wall tubular flow reactor operated at atmospheric pressure.

The paper is carbonized in inert atmosphere (He, 5 cm/s) at the following conditions: 1 K/min ramp up to 350 °C, 1 h dwell time, followed by 2 K/min ramp up to 850 °C and additional also 1 h dwell time.

$TiCl_4$ is used as a titanium source for converting C_b into TiC. It is vaporized in a bubbler and carried into the reactor by a carrier gas H_2 or He, dosed by mass flow controllers. The gaseous precursors diffuse into the pores of the carbon biotemplate, where reductive decomposition of $TiCl_4$ in excess of hydrogen and chemical reaction to TiC takes place simultaneously. The effect of the process parameters such as temperature (1000–1200 °C), gas flow velocity (5–18 cm/s), molar fraction of the precursor ($x_{TiCl_4} = 0.01 - 0.06$) and $H_2/TiCl_4$ molar ratio (7–55) on the mass gain and the porosity of the samples after infiltration is investigated. Three pieces of carbonized paper are infiltrated and converted into TiC ceramics in the isothermal zone of the reactor for each experiment.

Titanium oxide porous ceramics are produced by oxidation of TiC ceramics at 850 °C for 6 h in air flow (10 cm/s) in the same equipment.

The composition of the porous ceramics is determined by XRD and EDX. The X-ray diffraction spectroscopy (Phillips PW 3040) is performed with rotation of the samples and Cu Kα radiation in angle range $2\theta = 5$–$85°$. The morphology of the ceramics is investigated by Scanning Electron Microscopy coupled with an Energy Dispersive X-ray Analysis (SEM/EDX, JSM-6400) to determine the element distribution across the infiltrated layer. The porosity of the ceramics is determined by Hg-porosimetry (Carlo Erba Mercury Intrusion Porosimeter 2000).

According to German Standard Code DIN 52 292, coaxial double ring bending test (INSTRON Model 4204) is carried out to measure the bending strength of the ceramic specimen. A scheme of the experimental arrangement is presented in Fig. 2.

The bending strength σ_b of the specimen is related to the maximum load force F_{max} before crushing and the sample thickness s. For rectangular specimen, bending strength $\sigma_{b,max}$ is given by:

$$\sigma_{b,max} = 1.04 \frac{F_{max}}{s^2}.$$